Use of Stream Chemistry for Monitoring Acidic Deposition Effects in the Adirondack Region of New York

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ABSTRACT

Acid-neutralizing capacity (ANC) and pH were measured weekly from October 1991 through September 2001 in three streams in the western Adirondack Mountain region of New York to identify trends in stream chemistry that might be related to changes in acidic deposition. A decreasing trend in atmospheric deposition of SO_4^{2-} was observed within the region over the 10-yr period, although most of the decrease occurred between 1991 and 1995. Both ANC and pH were inversely related to flow in all streams; therefore, a trend analysis was conducted on (i) the measured values of ANC and pH and (ii) the residuals of the concentration–discharge relations. In Buck Creek, ANC increased significantly ($p < 0.05$) over the 10 yr, but the residuals of ANC showed no trend ($p > 0.10$). In Bald Mountain Brook, ANC and residuals of ANC increased significantly ($p < 0.01$), although the trend was diatonic—a distinct decrease from 1991 to 1996 was followed by a distinct increase from 1996 to 2001. In Fly Pond outlet, ANC and residuals of ANC increased over the study period ($p < 0.01$), although the trend of the residuals resulted largely from an abrupt increase in 1997. In general, the trends observed in the three streams are similar to results presented for Adirondack lakes in a previous study, and are consistent with the declining trend in atmospheric deposition for this region, although the observed trends in ANC and pH in streams could not be directly attributed to the trends in acidic deposition.

THE EFFECTS OF acidic deposition on lake chemistry in the Adirondack region of New York have been well established and continue to be well monitored. A lake survey in 1991–1994 showed that 41% of 1812 Adirondack lakes were either chronically acidic or susceptible to episodic acidification (Driscoll et al., 2001). However, a decreasing trend in acidic deposition dating back to 1978 suggests the potential for recovery of lake chemistry, and monitoring of 48 Adirondack lakes from 1992 to 2000 indicated that 29 of these lakes showed some increase in acid-neutralizing capacity (Driscoll et al., 2003). In contrast to this extensive database on lake chemistry, information on stream chemistry in the Adirondack region is limited. The USEPA Episodic Response Program provided detailed characterization of flow-related variations in chemistry for four Adirondack streams, from 1988 to 1990 (Wigington et al., 1996), but the only published data on stream chemistry in the region since 1990 are from two tributaries of an Episodic Response Program stream, monitored since 1998 (Lawrence, 2002), and an additional stream in the central Adirondack region, monitored since 1995 (McHale et al., 2000).

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The response of streams to acidic deposition can differ from that of lakes because streams are more directly influenced by soil, particularly during high flows that are often acidic. Stream water during baseflow may include a large fraction of water that has been neutralized by passing through till or bedrock (ground water), where the capacity for acid neutralization is greater than that in the soil (Chen et al., 1984). Storage of baseflow enables lakes to attenuate acidic inputs received during high stream flows. These factors result in greater short-term variability in the chemistry of streams than in lakes, and make monitoring of stream chemistry useful for providing information on soil conditions (for example, Likens et al., 1996; Lawrence et al., 1999; Lawrence, 2002), as well as on lotic habitat.

Additional information on stream chemistry in the Adirondack region has become available through the monitoring of three streams by the New York State Adirondack Lakes Survey Corporation, from 1991 to 2001. The three streams, which were formerly studied in the Episodic Response Program, were sampled weekly during this period to identify changes in stream water ANC and pH. We analyzed these data to determine (i) if significant changes in stream water ANC or pH have occurred during this 10-yr period, (ii) if trends in ANC or pH are related to specific seasons or changes in climate that led to trends in stream flow, and (iii) if changes in stream chemistry were consistent with changes in acidic deposition during this period.

MATERIALS AND METHODS

Site Information

Following the conclusion of the Episodic Response Program, the Adirondack Lakes Survey Corporation selected three of the study streams, Buck Creek, Bald Mountain Brook, and Fly Pond outlet, for continued sampling on a weekly basis (Fig. 1). The watersheds of these streams are characterized by rugged terrain. Forests are a mixture of northern hardwoods, including sugar maple (*Acer saccharum* Marshall), red maple (*Acer rubrum* L.), yellow birch (*Betula alleghaniensis* Britton), and American beech (*Fagus grandifolia* Ehrh.), and conifers, including balsam fir [*Abies balsamea* (L.) Mill], red spruce (*Picea rubens* Sarg.), and eastern hemlock [*Tsuga canadensis* (L.) Carrière]. Soils are thin (mostly classified as Spodosols) with well-developed organic surface layers (forest floor) more than 5 cm thick. The bedrock in this region is a complex mosaic that includes granitic and other forms of gneiss and metasedimentary rocks of varied mineral composition. The most recent glaciation deposited till of local and nonlocal origin, which varies in thickness and mineralogy, and has been determined to be an important factor in controlling water

Abbreviations: ANC, acid-neutralizing capacity.

chemistry in this region (Driscoll and Newton, 1985). Information on the spatial patterns of till mineralogy is not available for this region, however. The climate is characterized by cool summers, a growing season that extends from late May to early September, and cold winters with temperatures that remain below freezing on most days from December through mid March. Mean temperature in July is 18°C and in January is −10°C. Snow generally accumulates over the winter to maximum depths of between 0.5 to 1.5 m. Snowmelt most commonly occurs in April, and results in elevated stream flow through most of the month. Annual precipitation averages 1500 mm (Newton, 1990).

The watersheds of the three study streams occupy similar positions in the landscape (minimum elevations from 560 to 570 m; maximum elevations from 710 to 775 m). Second-order Buck Creek has the largest drainage area (3.1 km^2) and the steepest gradient (50 m km^{-1}), followed by first-order Bald Mountain Brook (area 2.2 km^2; gradient 25 m km^{-1}) and Fly Pond outlet (area 0.9 km^2; gradient 9 m km^{-1}), which is approximately 1 km downstream of Fly Pond. The Buck Creek watershed has one wetland (area of <3 ha) in a mid-elevation tributary watershed, but otherwise is well drained. Bald Mountain Brook runs through a narrow valley with poorly drained soils that are occasionally flooded. Stream flow within the watershed has been altered by beaver dams, which are periodically repaired. Approximately half of the watershed of Fly Pond outlet (defined by the sampling point) drains into Fly Pond, which is bordered by the only wetland (area of <3 ha) in the watershed.

Atmospheric deposition data for the study period were obtained from the National Atmospheric Deposition Program

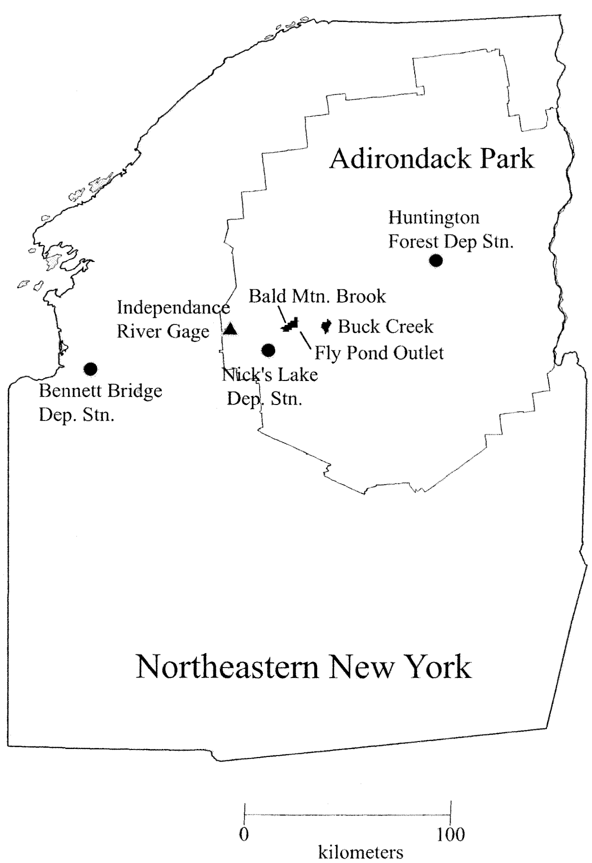

Fig. 1. Locations of study watersheds, stream gaging, and deposition monitoring stations used in this analysis.

(2003) for sites that bracket the western Adirondack region on the east (Huntington Forest) and west (Bennett Bridge), and from the New York State Atmospheric Deposition Monitoring Program (2003) that operates a site at Nick's Lake, approximately 10 to 30 km southwest of the study watersheds (Fig. 1).

Flow Measurement, Water Sampling, and Chemical Analysis

None of the streams had flow-gaging stations during the study period; therefore, stream-flow data from the U.S. Geological Survey gage on the Independence River at Donnattsburg, New York (Station 04256000) were used to evaluate effects of flow variations on stream chemistry. The Independence River gaging station (watershed area = 228 km^2) is 30 to 50 km west of the study streams (Fig. 1). The long-term record of flow (begun in 1942) and the record for the period of study (1991–2001) were used to determine if flow during the 1990s was unusual or if trends in flow during the 1990s were related to variations in chemistry.

Estimating flow of one stream from that of another is a standard approach used by the USGS to regionalize flow records (Riggs, 1973). The relation between the flow records of any two streams can vary, however, depending on the degree of similarity in watershed characteristics and variations in local precipitation and snowmelt patterns. Generally, the reliability of this approach is verified by comparing periods when flow records for both streams are available. The only flow data available in the study area to compare with the Independence River flow data were collected at Buck Creek from November 1988 to May 1990. Although the Buck Creek tributary drains a much smaller watershed (area = 3.1 km^2) than the Independence River, a statistically significant positive relation ($p <$ 0.001; $R^2 = 0.68$) in daily mean flows was observed between the two records (Fig. 2).

We also supported our assumption that flow patterns at Independence River were similar to the three study streams by relating the chemistry of the study streams to the flow of Independence River. A strong relationship between ANC or pH, and flow, is typically observed in Adirondack streams (Peters and Driscoll, 1987). Therefore, a strong relationship between flow at Independence River and the chemistry of the study streams would suggest that the flow record of the Independence River could be used to approximate the variation in flows of the study streams.

Water samples were collected weekly at each stream from 1 Oct. 1991 to 24 Sept. 2001 by manually filling a polyethylene bottle at streamside. Measurements of ANC were made by

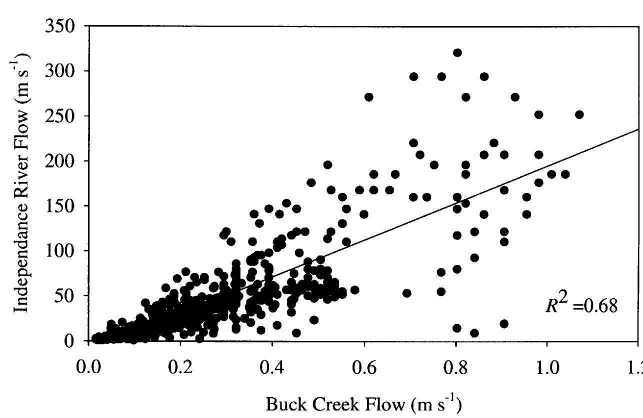

Fig. 2. Stream flow at Independence River as a function of stream flow at Buck Creek, November 1988 to May 1990.

Table 1. Chemical characteristics of the three study streams in the western Adirondack region of New York, 1991–2001.

	Mean of six monthly samples (January–June 2001)		
Constituent	Buck Creek	Bald Mountain Brook	Fly Pond outlet
pH	5.58	6.22	7.11
ANC†, μeq L^{-1}	16	52	251
		μmol L^{-1}	
SO_4^{2-}	60	54	52
NO_3^-	35	32	25
Cl^-	9.5	7.7	31
Ca^{2+}	51	50	136
Mg^{2+}	18	22	43
Na^+	40	47	95
K^+	7.1	7.5	15
DOC‡	327	220	330
Si	145	170	212
NH_4^+	<1	<1	1.7
Al, total monomeric	5.9	2.5	2.1
Al, inorganic monomeric	2.3	0.3	0.1

† Acid-neutralizing capacity.
‡ Dissolved organic carbon.

the Gran plot method and pH measurements were made with a glass electrode on air-equilibrated samples. Measurement procedures followed those established in the Episodic Response Program (Kretser et al., 1993). One sample from each stream was also collected monthly, from January 2001 through June 2001, and analyzed for the constituents listed in Table 1.

Statistical Analysis

Annual atmospheric deposition data from 1991–2000 were analyzed for trends (by calendar year) with the Mann–Kendall test, to enable comparison with the records of stream chemistry. The stream data for ANC and pH, for the period of October 1991–September 2001, were analyzed for trends through both linear regression and the seasonal Mann–Kendall test, which is most often chosen for this type of trend analysis. Regression techniques were used because (i) the data met the requirements of parametric tests and (ii) yearly and seasonal interactions could be evaluated in greater detail than possible with the nonparametric ranking approach of the seasonal Mann–Kendall test. To remove the variation in chemistry associated with changes in flow, ANC and pH measurements were plotted as a function of flow. Nonlinearity in these relations was reduced through application of logarithmic or hyperbolic transformations of flow data. A locally weighted scatterplot smoothing relation was then fitted to the data, from which residuals were calculated for each sampling date (Helsel and Hirsch, 1992). To reduce the influence of extreme values, the median of the four or five values measured each month (for uncorrected data and residuals) was then used for the regression analysis.

The seasonal Mann–Kendall test required that each month be considered an individual season, whereas the regression analysis allowed the grouping of months without further lumping of data. Five groups (seasons) were selected for the regression analysis on the basis of seasonal variability in flow, ANC or pH, and values of residuals. April was designated as a separate season to isolate the effects of snowmelt that clearly distinguished this month from all others in 9 of the 10 years. August and September were grouped because they tended to have the lowest flows and the highest ANC and pH values each year. May, June, and July were grouped because they represent the period of most rapid forest growth, and generally had higher flows than later in the growing season (August and September). October and November were grouped because flows typically increased through these months until the winter freeze. December, January, February, and March were grouped because air temperature generally remains below freezing during these months, and flows were relatively stable, except during occasional thaws.

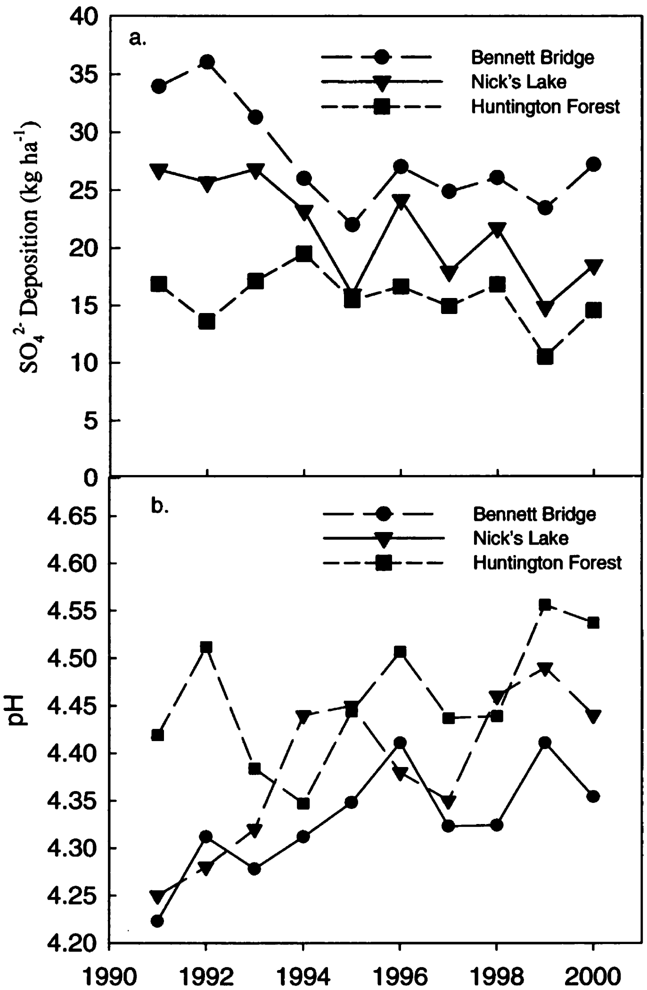

Fig. 3. Trends in (a) atmospheric wet deposition of SO_4^{-2} and (b) pH from 1991 to 2000 at three sites located in Fig. 1.

For multiple linear regression analysis, season was treated as a categorical variable and year was treated as a continuous variable. The regression models included the two main effects (season and year) as well as their interactive effect, which tested the parallelism of the yearly trends for different seasons. The validity of using linear regression was checked by a test for normality and evaluation of the plots of residuals versus predicted values.

RESULTS

Characterization of Current Stream Chemistry

Monthly pH values from January to June 2001 indicated that, at base flow, Buck Creek was acidic, Bald Mountain Brook was moderately well buffered, and Fly Pond outlet was well buffered (Table 1). In general, values of ANC less than 50 μmol_c L^{-1}, pH less than 6.0, and inorganic Al concentrations greater than 2.0 μmol L^{-1} indicate that aquatic biota are at risk from acidification (Driscoll et al., 2001). Concentrations of dissolved organic carbon were similar among the three streams,

Table 2. Annual mean and percentage of flows that exceeded the listed value for each period of analysis for the Independence River at Donnattsburg, New York.

Analysis period	Annual mean	Percent of flows exceeded by the listed value† 10%	50%	90%
	$m^3\ s^{-1}$			
1942–2000 (continuous record)	5.58	11.8	3.40	1.19
Study period, 1991–2001 (continuous record)	5.83	11.9	3.43	1.44
522 Sampling dates from 1991 to 2001	5.86	12.6	3.40	1.44

† For example, daily mean flows exceeded 11.8 $m^3\ s^{-1}$ 10% of the days from 1942–2000.

but were lowest in Bald Mountain Brook. Concentrations of Si were lowest in Buck Creek and highest in Fly Pond outlet. The higher concentrations of Na and Cl in Fly Pond outlet than in the other streams are probably the result of winter salt applications to deice the road that intersects the stream within the watershed.

Atmospheric Deposition and Stream Flow in the 1990s

Annual wet deposition of SO_4^{2-} in the northeastern United States has been generally decreasing since a peak in the early-to-mid 1970s (Driscoll et al., 2001). At the three deposition monitoring sites closest to the watersheds (Fig. 1), annual rates of SO_4^{2-} deposition decreased during the 1990s (Fig. 3), although the trend for this 10-yr period was statistically significant ($p < 0.05$) only at one site (Nick's Lake). The pH of wet deposition increased at all three sites during the 1990s; statistically significant at Nick's Lake and Bennett Bridge, where most of the increase occurred from 1991 to 1995 (Fig. 3).

To determine if flow during the 1990s was unusual, the continuous record during the analysis period (October 1991–September 2001) and the flows recorded on days when samples were collected were compared with the complete 58-yr record at the Independence River gage. The annual mean (computed from daily mean flows) and the flow values that were exceeded by 10, 50, and 90% of the mean daily flows were similar for the complete record, the continuous record during the analysis period, and the flows during sampling days (Table 2). The higher values during the 1990s for the flow value exceeded by 90% of daily mean flows indicate that the 1990s were, in general, somewhat wetter than the long-term record. The similarity between the continuous record for the study period and the flows on sampling days, indicates that sampling frequency was sufficient to avoid potential bias in the flow data that represented the sampling dates (Table 2).

No trend is evident in the daily mean flows of the 1990s, even though the frequency of extremely low flows, and to a lesser extent, extremely high flows, was greater in the second half of the decade than in the first half (Fig. 4a, 4b). Flows on sampling dates that exceeded 30 $m^3\ s^{-1}$ occurred eight times from April 1996 to April 2001, but did not occur before April 1996. Flows less than 1 $m^3\ s^{-1}$ did not occur before June 1995, but occurred on 20 sampling dates from June 1995 to September 2001. Removing all flows greater than 1.5 $m^3\ s^{-1}$ from the record resulted in a significant decrease ($p < 0.001$) in the continuous flow record over the study period.

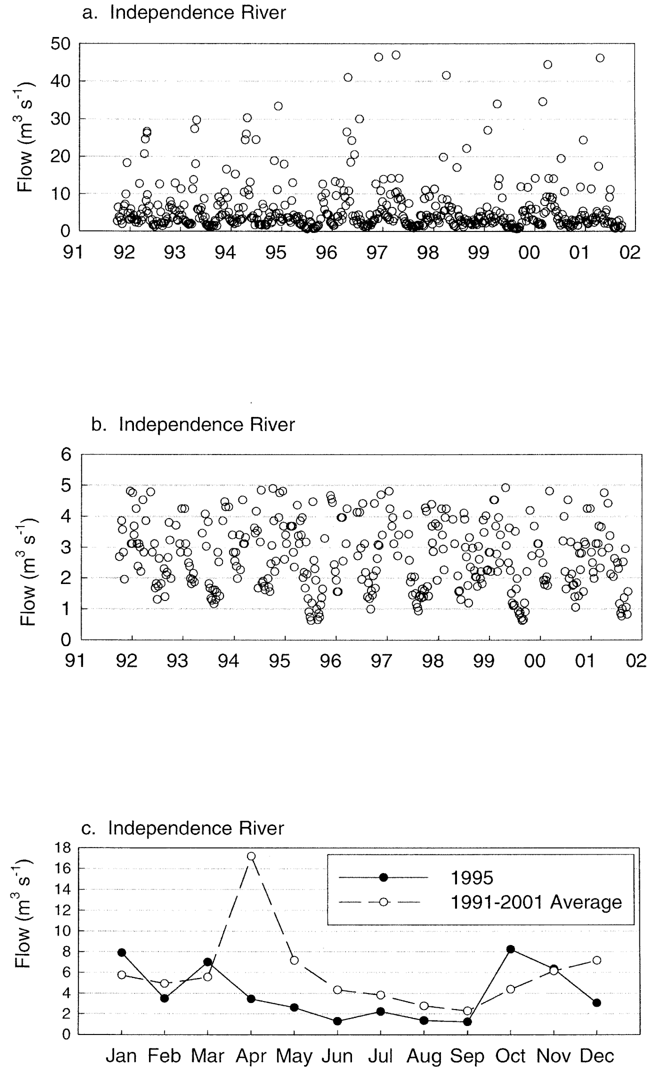

Fig. 4. (a) Mean daily stream flow at the Donnattsburg gage on the Independence River, on days when stream samples were collected for chemical analysis. (b) Flow record in (a) for values less than 5 m s^{-1}. (c) Mean daily flow at the Donnattsburg gage averaged by month for the entire study period and for 1995.

The seasonal pattern of flow is characterized by a pronounced peak in April that is caused by melting snow that accumulates over the winter, and a late summer minimum that results from a soil moisture deficit that develops over the course of the growing season from evapotranspiration (Fig. 4c). Flow tends to increase in the fall after the growing season, and then remains relatively stable during the winter months.

Trends in Stream Water Acid-Neutralizing Capacity

In all three streams, ANC decreased with increases in flow (Fig. 5). The curvilinearity of the relationship

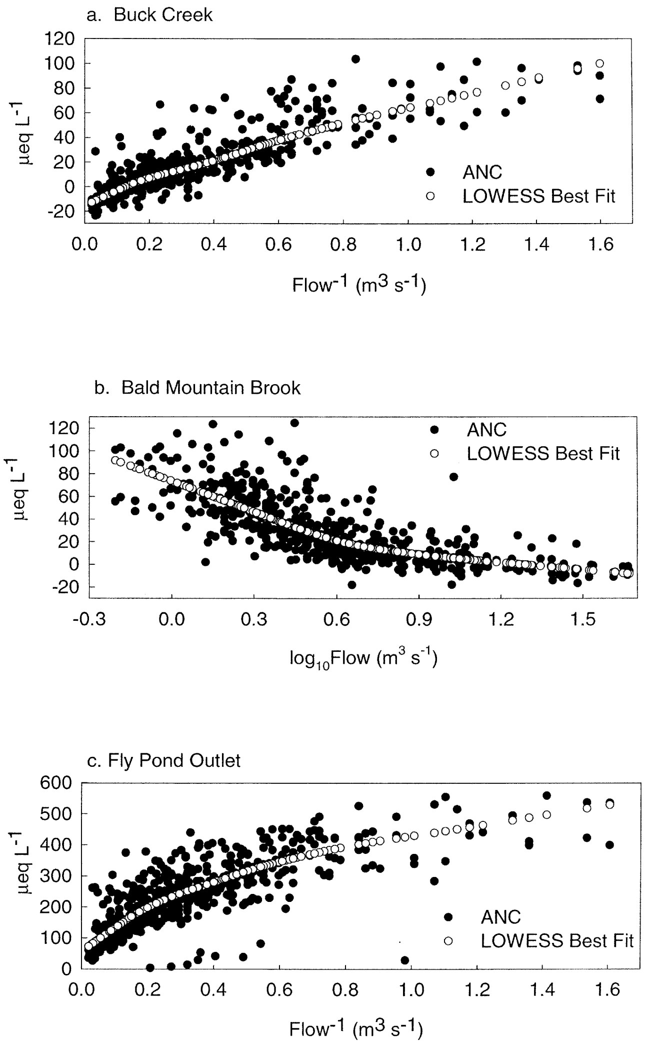

Fig. 5. Acid-neutralizing capacity (ANC) as a function of mean daily flow at (a) Buck Creek (transformed to flow^{-1}), (b) Bald Mountain Brook (transformed to $\log_{10}$ flow), and (c) Fly Pond outlet (transformed to flow^{-1}).

for Buck Creek was reduced when ANC was plotted against flow^{-1} (Fig. 5a). This transformation of flow data enabled unbiased fitting of the locally weighted scatterplot smoothing (LOWESS) line. For Bald Mountain Brook, the $\log_{10}$ transformation of flow data yielded the best fit of the LOWESS line; however, some bias in the fit existed as a result of divergent ANC values at the lowest flows (Fig. 5b). The best fit of the LOWESS line was obtained for data from the Fly Pond outlet after transforming flow to flow^{-1} (Fig. 5c).

Linear regression yielded the same results as the seasonal Mann–Kendall test for statistical significance of ANC trends. Monthly median ANC values ranged from -22.1 to 97.6 $\mu mol_c\ L^{-1}$ during the 10-yr record for Buck Creek. A statistically significant ($p < 0.05$) increasing ANC trend (1.5 $\mu mol_c\ L^{-1}\ yr^{-1}$) was observed when effects of flow variations were not removed (uncorrected), but no trend was observed in the residuals of the ANC–flow^{-1} relation (Fig. 6a, 6b). In Bald Mountain Brook, in which ANC ranged from -12.9 to 116 μmol_c L^{-1}, an increasing trend with time was observed for

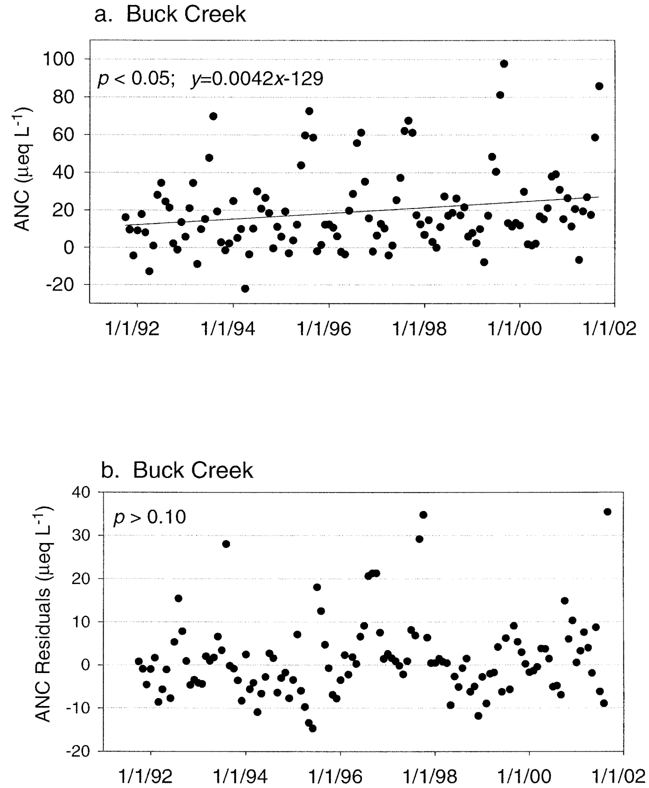

Fig. 6. Trends in (a) acid-neutralizing capacity (ANC) and (b) residuals of the ANC–flow relation for the study period at Buck Creek.

both the uncorrected data (3.3 $\mu mol_c\ L^{-1}\ yr^{-1}$) and the residuals of the ANC–$\log_{10}$ flow relation (Fig. 7a, 7b). However, the residuals showed a distinct decreasing trend from 1991–1995 that changed to a pronounced increase from 1996 to 2001 (Fig. 7b). Fly Pond outlet, the most well buffered of the three streams, showed the greatest range in ANC values (59.7 to 525 $\mu mol_c\ L^{-1}$), and exhibited a statistically significant increasing trend in both ANC values (10.6 $\mu mol_c\ L^{-1}\ yr^{-1}$) and residuals of the ANC–flow^{-1} relationship (Fig. 8a, 8b).

Interaction between year and season was statistically quantified for both ANC and residuals of ANC to determine if trends during 1991–2001 would be observed in some seasons but not in others. This interaction was only significant for Bald Mountain Brook data (ANC and residuals of ANC). To identify trends within seasons, simple linear regression was performed on the relation between time and ANC residuals for each season, separately (Table 3). None of the streams showed statistically significant increases for all seasons, although increases were observed in four of the five seasons in Fly Pond outlet ($p < 0.05$). All three streams showed significant increases in December, January, February, and March ($p < 0.05$) and in April ($p < 0.10$). Negative trends in ANC did not occur in any streams during any seasons.

Trends in Stream Water pH

As for ANC, linear regression yielded the same results as the seasonal Mann–Kendall test for statistical

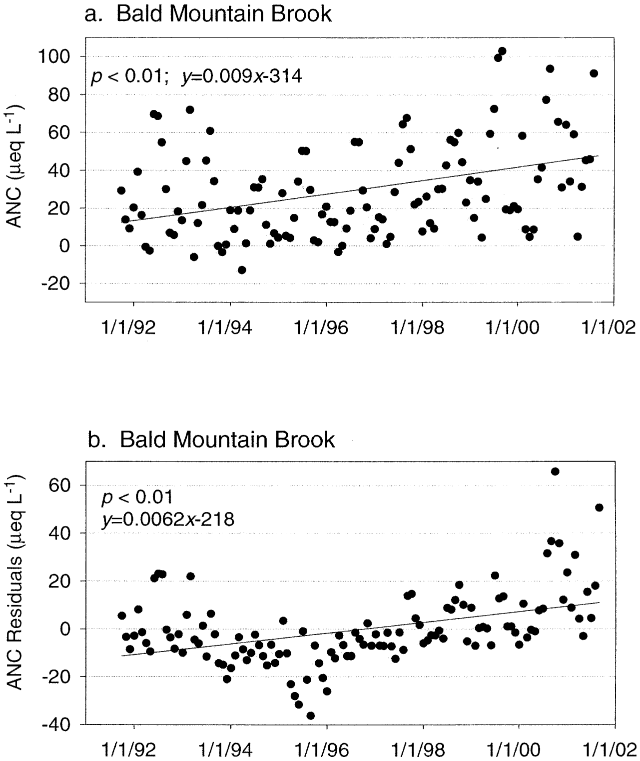

Fig. 7. Trends in (a) acid-neutralizing capacity (ANC) and (b) residuals of the ANC–flow relation for the study period at Bald Mountain Brook.

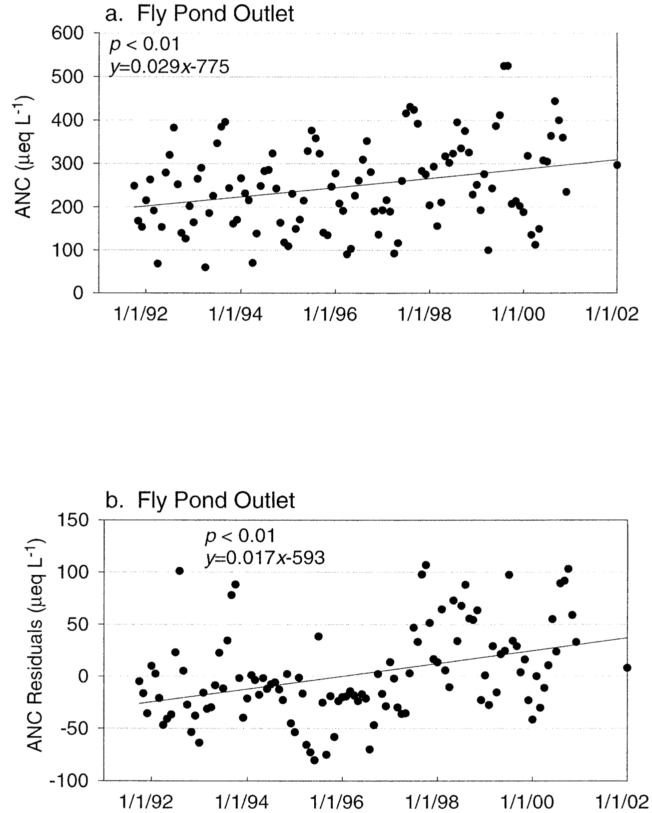

Fig. 8. Trends in (a) acid-neutralizing capacity (ANC) and (b) residuals of the ANC–flow relation for the study period at Fly Pond outlet.

significance of pH trends. The relations between pH and flow were similar to those of ANC and flow: decreased pH with increased flow. Therefore, the residuals of pH were determined by the identical procedures as for the ANC residuals. Trends in pH at the three sites were similar to the ANC trends. Monthly median pH values for Buck Creek ranged from 4.66 to 7.13 during the study period, but no statistically significant trends ($p < 0.05$) were observed in either pH or the residuals of pH for Buck Creek, although an increasing trend in pH (0.016 pH units yr^{-1}) was observed for $p < 0.10$. The pH range for Bald Mountain Brook (4.85–7.25) was similar to Buck Creek; however, both pH (0.077 pH units yr^{-1}) and residuals of pH increased ($p < 0.05$) over the study period. Residuals of pH for Bald Mountain Brook showed a decrease from 1991–1995 and increase from 1995 to 2001, similar to that observed for ANC. The pH values for Fly Pond outlet ranged from 6.32 to 7.89, and increased significantly ($p < 0.05$) at a rate of 0.032 pH units yr^{-1} over the study period. Residuals of pH also increased significantly ($p < 0.05$).

The interaction between year and season was only significant for Bald Mountain Brook, for which significant increases in the residuals of pH were observed in all seasons except April (Table 3). Buck Creek residuals showed no trends in any of the seasons, whereas increasing trends were observed for Fly Pond outlet in all seasons except late summer (Table 3).

DISCUSSION

Effects of Flow Variations on Stream Chemistry

Similar increasing trends in ANC and pH measurements were observed for 1991–2001 in all three streams, but these trends changed uniquely for each stream when the effect of flow variation was removed. In Buck Creek, the increasing trends that were detected in ANC ($p < 0.05$), and possibly pH ($p < 0.10$), were no longer observed if the effect of flow variation was removed. In Bald Mountain Brook, removal of flow variations resulted in a distinct downward trend from 1991 to 1995, followed by a pronounced upward trend in ANC from 1996 to 2001. Removal of flow variation in Fly Pond

Table 3. Presence or absence of statistically significant increasing trends in the residuals of concentration–discharge relationships ($p < 0.05$) by season in the three study streams from 1991–2001.†

	Season				
Stream	**April**	**May–July**	**August–September**	**October–November**	**December–March**
Buck Creek	–	–	–	–	**ANC**
Bald Mountain Brook	–	**pH**	**ANC, pH**	**ANC, pH**	**ANC, pH**
Fly Pond outlet	**ANC, pH**	**ANC, pH**	**pH**	**ANC**	**ANC, pH**

† Significant increasing trends ANC (acid-neutralizing capacity) or pH are indicated by "ANC" or "pH." No decreasing trends were detected.

outlet changed the gradual, 10-yr increase in uncorrected ANC values to the abrupt increase observed in residuals in 1997, but no clear trend before or after this year. The pH trend in Fly Pond outlet, however, was similar in both the uncorrected data and the residuals. Comparison between the measured data and the residuals therefore indicates the importance of long-term flow data for interpreting trends in stream chemistry.

Comparison with Trends of Adirondack Lakes

In general, the trends observed in the three streams are similar to results presented for Adirondack lakes by Driscoll et al. (2003), and are consistent with the declining trend in atmospheric deposition for this region. However, the observed trends in ANC and pH in streams could not be directly attributed to the trends in acidic deposition. Time-dependant watershed processes such as mineral weathering, cation exchange, and mineralization of organic matter are likely to influence the response of surface water chemistry to decreasing deposition in ways that are not fully understood, and may result in differing responses between lakes and streams. For example, most of the lakes that showed a significant increase in ANC in the study of Driscoll et al. (2003) were in watersheds considered to have thin till underlying soils, whereas the stream that exhibited the largest ANC increase (Fly Pond outlet) was most likely in a watershed that contained thick till deposits. Buck Creek, whose watershed is likely to have thin till, exhibited little or no change in ANC.

Effects of Local Hydrology

The strong relations between ANC and flow in Fig. 5 confirmed that the Independence River reflected general climatic fluctuations for the region and, therefore, was useful in evaluating trends in the study streams. However, the difference in size and location between the Independence River and the study streams undoubtedly resulted in some degree of error. In Buck Creek, the wide variations in pH and ANC of stream water probably reflected the influence of deep flow paths through neutralizing till during low flows, and shallow flow paths through relatively acidic soil during high flows (Chen et al., 1984). Acidic conditions during high flows are a strong indication that soils in the Buck Creek watershed were ineffective at buffering inputs of acidic deposition and are likely to have experienced Ca depletion (Lawrence, 2002). In this type of watershed, climatic fluctuations that affect stream flow can, therefore, also affect trends in stream chemistry, as shown in Buck Creek, where increased frequency of low flows in the second half of the decade resulted in a trend in ANC and pH that was not evident after the effect of flow variations was removed.

In Bald Mountain Brook, removal of the effects of flow variations accentuated a diatonic trend that was not observed in the other two study streams. Absence of a substantial snowmelt followed by dry conditions throughout the summer (Fig. 4c) may have led to an accumulation of mineralized S and N, and associated acidity in the riparian wetland soils of this watershed. Occasional, small increases in flow may have therefore been more acidic than normally occurs at those flow levels. This process was documented in a previous study of tributary watersheds in Buck Creek (Lawrence, 2002). Minimum residual values also occurred in Buck Creek and Fly Pond outlet during the summer of 1995, but were perhaps less pronounced because these watersheds contain less wetland area than Bald Mountain Brook. Extensive beaver dams, verified in the Bald Mountain Brook watershed through ground surveys in 1990 and aerial photography in 1998, may also have complicated the chemical record. Changes in ANC and pH have been attributed to changes in hydrologic conditions created by beaver ponds in the Adirondack region (Driscoll et al., 1987; Cirmo and Driscoll, 1993).

The considerably higher ANC and pH in Fly Pond outlet than in the other two study streams suggests the presence of till that provides ground water flow paths where acid buffering can occur. Higher concentrations of Si in Fly Pond outlet than in the other two streams are consistent with extended contact time with Si-based minerals that provide acid neutralization through weathering, and may be a result of the mineralogy of parent material, as well as extended ground water residence times provided by till. The abrupt shift in 1997 from negative values of ANC residuals (and to a lesser extent pH residuals) to positive values suggests a rapid change in environmental conditions, but an explanation for this response is not clear. A contributing factor may have been the effect of Fly Pond, which would tend to attenuate and delay the stream's responses to precipitation. The use of daily mean flows from the Independence River could, therefore, introduce some error in the relations between stream chemistry and discharge in Fly Pond outlet. Nevertheless, much of the variability in ANC and pH was accounted for by flow variations measured in the Independence River (Fig. 4c), as was observed for the other two streams.

CONCLUSIONS

The increasing trends in the ANC and pH generally corresponded to trends of decreasing acidic deposition in all three streams, if the data were uncorrected for flow variation. Although the trends in uncorrected stream chemistry were not driven by any particular season, these relations were changed by the removal of the effects of flow variations. The weak trend in ANC in the uncorrected data from Buck Creek was probably related to an increased frequency of extremely low flows in the latter part of the record. Had flow been monitored on Buck Creek, effects of flow variation on trends in stream chemistry could have been removed with greater precision, thereby increasing the sensitivity of the analysis for detecting trends. Nevertheless, this result emphasizes the importance of continuous flow records in assessing long-term trends in stream chemistry, and suggests that reversal of acidification has been minimal in this watershed.

Residuals of ANC in Bald Mountain Brook show diatonic trends that decreased during the period that acidic deposition decreased the most rapidly, an apparent inconsistency that could be the result of a lagged response. The mechanism for such a response, however, is not clear. The abrupt increase in flow-adjusted ANC in Fly Pond outlet in 1997 is also not directly linked to the acidic deposition trends.

The inconsistent relationships between the deposition trend and the stream trends limit conclusions regarding the recovery status of these streams, although the trend analysis does indicate that at least two of the streams are less acidic than 10 yr ago. Nevertheless, these data represent the only continuous stream monitoring conducted in the Adirondack region over the past decade. Values of ANC that decrease to levels near or below 0 $\mu mol_c\ L^{-1}$ during high flows in the recent record of Buck Creek and Bald Mountain Brook indicate that (i) these streams continue to experience episodic acidification at levels that harm fish populations and (ii) the soils in the watersheds of these streams provide limited buffering. In contrast, the high ANC and high Ca concentrations of Fly Pond outlet indicate that this stream continues to provide suitable chemistry for fish habitat, as observed in 1988–1990 in the Episodic Response Program (Baker et al., 1996).

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